

PTO 07-[0293]

Japanese Patent

Sho 47-31924

**METHOD FOR MANUFACTURING SODA ACRYLATE OR SODA METHACRYLATE  
POWDER CRYSTAL**

[Akurirusan Soda Matawa Metaakurirusan Soda Bunmatsu Kessho No  
Seizoho]

Hiroo Ito, Migiho Morita, and Yasutada Inakuma

UNITED STATES PATENT AND TRADEMARK OFFICE

Washington, D.C.

November 2006

Translated by: Schreiber Translations, Inc.

Country : Japan

Document No. : Sho 47-31924

Document Type : Kokai

Language : Japanese

Inventor : Hiroo Ito, Migiho Morita, and  
Yasutada Inakuma

Applicant : Toagosei Chemical Industry Co.,  
Ltd.

IPC : 16 B 631.11

Application Date : April 6, 1971

Publication Date : November 14, 1972

Foreign Language Title : Akurirusan Soda Matawa  
Metaakurirusan Soda Bunmatsu  
Kessho No Seizoho

English Title : METHOD FOR MANUFACTURING SODA  
ACRYLATE OR SODA METHACRYLATE  
POWDER CRYSTAL

## Specification

1. Title of the invention

Method for Manufacturing Soda Acrylate or Soda Methacrylate  
Powder Crystal

2. Claim

A method for manufacturing a soda acrylate or soda metharylate powder crystal, characterized by the fact that an aqueous soda acrylate or soda methacrylate solution is sprayed and dried at a drying temperature of 80-200°C.

3. Detailed explanation of the invention

The present invention pertains to a method for obtaining a powder crystal of soda acrylate or soda methacrylate from an aqueous solution of soda acrylate or soda methacrylate. Its purpose is to obtain a useful powder crystal as a synthetic raw material of various kinds of acrylic acid or methacrylic acid esters by drying an aqueous solution of soda acrylate or soda

---

<sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

methacrylate in a short time without generating a polymerized product.

As for the soda acrylate or soda methacrylate, in order to obtain a crystal of soda acrylate or soda methacrylate by neutralizing acrylic acid or methacrylic acid with an aqueous caustic soda solution, a method for separating a parent solution by a filtration or a centrifugal separation operation of the crystal of soda acrylate or soda methacrylate being enriched and precipitated has been adopted.

However, in case these operations are carried out, since the soda acrylate or soda methacrylate is a very unstable monomer, the polymerization due to a heat is distinct, it is necessary to carry out the operations at low temperature in the presence of a large amount of polymerization preventive agent, and drying must be carried out under reduced pressure for a long time. Furthermore, since the crystal of soda acrylate or soda methacrylate is a very infinitesimal amount, filtration, centrifugal separation operation, etc., are difficult, and it is very difficult to obtain a high-purity soda acrylate or soda methacrylate.

On the other hand, a powder-shaped soda acrylate or soda methacrylate is also obtained by an azeotropic dehydration of the water generated by neutralizing acrylic acid or /2

methacrylic acid with an organic solvent in the presence of a polymerization preventive agent. However, in this method, since the separation of the crystal and the parent solution was very difficult and the treatment method of the organic solvent also became a problem, this method was inefficiently, economically insufficient. An excellent powder crystal was difficult to be obtained by any of the above methods.

These inventors researched these drawbacks in earnest to improve and correct them, and as a result, it was discovered that a [illegible] powder with excellent purity was obtained at one time by spraying and drying an aqueous soda acrylate or soda methacrylate solution at a drying temperature of 80-200°C. Then, the present invention was completed.

The spraying and drying in the present invention can be applied by a general spray dryer, and the spraying and drying temperature of 80-200°C indicates the inner surface temperature of the dryer being used.

According to the method of the present invention, a nearly anhydrous crystal can be obtained in a short time at one time without filtration, centrifugal separation operation, etc., and this method is also economically very excellent. Furthermore, the soda acrylate or soda methacrylate can be stably dried with little polymerization, even at a high temperature of 80-200°C,

wherein it has not been able to exist stably, and water in the crystal obtained can be easily removed by [illegible], vacuum drying, etc. The reason why the soda acrylate or soda methacrylate that has been stable [illegible] at high temperature can be obtained as a crystal without polymerizing is uncertain, however it is considered that in the soda acrylate or soda methacrylate sprayed into a hot air, water is instantly evaporated and dried in a dryer, so that a solid soda acrylate or soda methacrylate is formed. In the solid soda acrylate or soda methacrylate, the polymerization due to the heat is very slow, compared with an aqueous solution, and the contact time with the heat is very short. Also, the water content in the crystal can be regulated by the operation conditions of the spray dryer, that is, the temperature in the dryer, the amount of hot air, and the amount of raw material being supplied, and the temperature in the dryer is required to be maintained in a temperature of 80-200°C. If the temperature is lower than 80°C, drying is insufficient, and a powder crystal cannot be drawn out. Also, if the temperature is higher than 200°C, a polymerized product is generated.

The method of the present invention can be appropriately applied according to the processes shown in Figure 1. In other words, an aqueous soda acrylate or soda methacrylate solution is

quantitatively supplied through a pipe 1 to the upper part of an atomizer, and a hot air heated by a heater is fed in a tangential direction with the main body into the upper part from a pipe 2. The aqueous soda acrylate or soda methacrylate solution is flown in an atomized shape in the dryer body, and the water is removed by the hot air while it is dropped to the lower part from the upper part of the dryer body, so that a crystal is drawn out of the lower part 4 of the body. The hot air is passed through an outlet 5 and discharged from a blower 7 after recovering an accompanying powder crystal by a cyclone 6.

Since the soda acrylate or soda methacrylate powder crystal obtained in the above-mentioned method of the present invention is finer than those obtained by other methods and the content of the polymerized product is a small amount, the powder crystal can be used in various kinds of usages. In particular, this powder crystal is appropriately used in the following usages.

In other words, the above-mentioned soda acrylate or soda methacrylate powder crystal is reacted at a temperature of 50-160°C with a halide such as [illegible], 2-methyl[illegible]hydrin, allyl chloride, methallyl chloride, and benzyl chloride, using a nonreactive organic solvent (aromatic hydrocarbons such as benzene, toluene, and xylene, aliphatic hydrocarbons such as n-hexane, n-heptane, and n-octane, tertiary

alcohols such as tert-butyl alcohol and tert-amyl alcohol, ethers such as propyl ether, isopropyl ether, butyl ether, tetrahydrofuran, and dioxane, polar solvents such as N,N'- /3 dimethylformamide, dimethyl sulfoxide, and [illegible]nitrile, chlorine group organic solvents such as carbon tetrachloride) and a catalyst (quaternary ammonium salts such as triethylbenzyl ammonium chloride and tetraethyl ammonium chloride, tertiary amines such as triethylamine and tributylamine, etc.) in the presence of a polymerization preventive agent (phenyl- $\alpha$ -naphthylamine, N,N'-diphenyl-p-phenylenediamine, hydroquinone, phenothiazine, sulfur, etc.), so that an ester of acrylic acid or methacrylic acid can be attained.

In this case, since the esterification reaction [illegible] the existence of water, the raw material soda acrylate or soda methacrylate being used is required to have a small amount of water and to be a fine powder. However, in the soda acrylate or soda methacrylate powder crystal obtained in the method of the present invention is suitable for these conditions as mentioned above, and a high-purity ester can be obtained with high yield by considerably favorably acting on the esterification reaction.

Next, the present invention is explained in detail by application examples, comparative examples, and referential



examples of the esterification using the powder obtained by the method of the present invention, and part means part by weight.

#### Application Examples 1-9 and Comparative Examples 1 and 2

A dryer body was heated in advance by sending a hot air into it, and an aqueous solution containing hydroquinone monomethyl ether at 0.0016 part by weight and soda acrylate or soda methacrylate at 60 parts by weight was quantitatively supplied. From the lower part of the dryer body, soda acrylate or soda methacrylate crystals were quantitatively obtained. The drying conditions and the analyzed values of the products are shown in Table I.

Table I

No.	原料液 給量 kg/hr	乾燥器 内温度 ℃	結晶分析値 (%)			備 考
			水分	アクリル酸 残存率 %	セリシ 酸残存率 %	
1	5.0	240	60	-	-	母液として 取り出す
2	5.0	120	80	49.7	50.04	0.26
3	5.0	120	100	51.4	59.50	0.50
4	5.0	120	120	60.0	59.72	0.28
5	5.0	120	140	27.8	71.89	0.51
6	5.0	120	150	16.0	99.51	0.09
7	5.0	120	150	0.45	99.20	0.55
8	5.0	100	180	0.57	98.12	1.51
9	5.0	100	220	0.51	92.56	7.15
比較例 1	濃縮液 100℃		0.12	89.40	10.48	アクリル酸 シラ
比較例 2	濃縮液 100℃		0.21	88.94	10.85	

1. Amount of raw material supplied, kg/h
2. Amount of hot air, m<sup>2</sup>/h
3. Temperature in the dryer, °C
4. Analyzed values of crystal (%)
5. Remarks
6. Water
7. Soda acrylate or soda methacrylate
8. Its salt and polymer
9. Cannot be drawn out as a crystal.
10. Application Example
11. Comparative Example
12. Enrichment temperature, 100°C
13. Soda acrylate
14. Soda methacrylate
15. Soda acrylate
16. Soda acrylate

(Note) (1) In Comparative Examples 1 and 2, the above-mentioned aqueous solution was enriched to [illegible] by the enrichment

method, and the crystal was filtered and dried under vacuum.

The heating time was 3 h.

(2) Water [illegible] based on the dry weight method.

(3) As the analysis method of the soda acrylate or soda methacrylate, a bromo method was adopted, and the analyzed values were calculated as  $(R=H_2CH_3)$ .

(4) In Application Example 2, only the surface of the aqueous soda acrylate or soda methacrylate solution was instantly dried in the dryer, and the internal water was diffusion-controlled and exists in a left state in the crystal. Thus, even if the water was 69.7%, a crystal was attained.

#### Referential Example 1

Using the soda acrylate obtained in Application Example 6, its esterification was carried out by the following prescription.

Dimethylformamide	200 cc
Soda acrylate	94 g
Methallyl chloride	90.5 g
Triethylamine	1.8 g
Phenoxazine	0.1 g

The above-mentioned amount was put into a flask, and the temperature was raised while stirring. The reaction was carried out at 100°C for 4 h, and cooling was carried out. The table salt generated was filtered and washed with dimethylformamide, and the filtrate was enriched under reduced pressure, [illegible], so that methallyl acrylate was obtained at a yield of 87%. The properties of the product were as follows. /4

Boiling point: 40°C/13 mmHg, and purity: 98.3%.

#### Referential Example 2

Using the soda methacrylate obtained in Application Example 7, its esterification was carried out by the following prescription.

Epichlorohydrin	462.5 g
Soda methacrylate	108 g
Triethylbenzyl ammonium chloride	2.3 g
Phenoxazine	0.1 g

The reaction and the posttreatment were carried out similarly to Referential Example 1, and the table salt crystal was washed with epichlorohydrin. Glycidyl methacrylate was obtained at a yield of 85%. The properties of the product were as follows.

Boiling point: 75°C/10 mmHg, and purity: 98.1%

4. Brief description of the figure

Figure 1 is a drying process diagram showing an embodiment of the present invention.

- 1 Raw material supply pipe
- 2 Hot air supply pipe
- 3 Blower
- 4 Crystal drawing-out port
- 5 Hot air outlet pipe
- 6 Cyclone
- 7 Blower

